OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

R&T CODE: 4133032

TECHNICAL REPORT NO. 83

Transition Metal Chelate-Fulleride Compounds: Electrocrystallization of Semiconducting $[Ru(bpy)_3](C_{60})_2$

by

C. A. Foss, Jr., D. L. Feldheim, D. R. Lawson, P. K. Dorhout, C. M. Elliott, C. R. Martin and B. A. Parkinson

Prepared for publication

in

Inorganic Chemistry

Department of Chemistry
Colorado State University
Ft. Collins, CO 80523

February 22, 1993

REPORT DOCUMENTATION PAGE

OMB No 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	Feb 1992	Interim

4. TITLE AND SUBTITLE
Transition Metal Chelate-Fulleride Compounds: Electrocrystallization of Semiconducting $(Ru(bpy)_3)(C_{60})_2$

5. FUNDING NUMBERS
Contract
N00014-82K-0612

6. AUTHOR(S)
C. A. Foss, Jr., D. L. Feldheim, D. R. Lawson, P. K. Dorhout, C. M. Elliott, C. R. Martin and B. A. Parkinson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Dr. Charles R. Martin
Department of Chemistry
Colorado State University
Fort Collins, CO 80523

8. PERFORMING ORGANIZATION REPORT NUMBER
ONR TECHNICAL REPORT # 83

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
Two recent breakthroughs in the chemistry of fullerenes have provided the impetus for using fullerenes to prepare novel solid state materials: a method to produce large amounts of C_{60} and related materials, and the discovery of superconductivity in fullerides of K, Rb and Cs. The superconducting alkali metal compounds, which appear to contain C_{60}^{3-}, show a trend toward higher transition temperatures upon increasing the size of the unit cell up to the composition Rb_2CsC_{60}. We thought that the synthesis of new compounds of reduced fullerenes with large cations might produce materials with interesting properties. Transition metal complexes with neutral chelating ligands (e.g. $Ru(bpy)_3^{2+}$, where bpy = 2,2' bipyridine) seemed like good candidates as cations for C_{60} salts. Such complex cations have a rich electrochemistry and photochemistry. Furthermore, the electronic and optical properties can be varied via ligand and metal substitution, providing a route for tuning the properties of the new materials. In addition, these complex cations can have dimensions comparable to the C_{60} molecule, perhaps allowing packing of the cations and the fullerene anions into classical ionic structures such as rock salt, CaI_2 or CaF_2. In this report, we describe our first efforts toward the preparation of such compounds with the synthesis of $(Ru(bpy)_3)(C_{60})_2$ which we find has a surprisingly high electrical conductivity.

14. SUBJECT TERMS
C_{60}, Fullerenes, charge transfer salts

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
		UNCLASSIFIED	

Transition Metal Chelate-Fulleride Compounds: Electrocrystallization of Semiconducting $[Ru(bpy)_3](C_{60})_2$

Colby A. Foss, Jr., Daniel L. Feldheim, Del R. Lawson, Peter K. Dorhout*, C. Michael Elliott*, Charles R. Martin*, and Bruce A. Parkinson*

Department of Chemistry
Colorado State University
Fort Collins, CO 80523

*Corresponding Authors.

Two recent breakthroughs in the chemistry of fullerenes have provided the impetus for using fullerenes to prepare novel solid state materials: a method to produce large amounts of C_{60} and related materials (1), and the discovery of superconductivity in fullerides of K, Rb and Cs (2). The superconducting alkali metal compounds, which appear to contain C_{60}^{3-}, show a trend towards higher transition temperatures upon increasing the size of the unit cell up to the composition Rb_2CsC_{60} (3). We thought that the synthesis of new compounds of reduced fullerenes with large cations might produce materials with interesting properties. Transition metal complexes with neutral chelating ligands (e.g. $Ru(bpy)_3^{2+}$,where bpy = 2,2' bipyridine) seemed like good candidates as cations for C_{60} salts. Such complex cations have a rich electrochemistry and photochemistry (4). Furthermore, the electronic and optical properties can be varied via ligand and metal substitution (4), providing a route for tuning the properties of the new materials. In addition, these complex cations can have dimensions comparable to the C_{60} molecule (5), perhaps allowing packing of the cations and the fullerene anions into classical ionic structures such as rock salt, CaI_2 or CaF_2. In this report, we describe our first efforts towards the preparation of such compounds with the synthesis of $[Ru(bpy)_3](C_{60})_2$ which we find has a surprisingly high electrical conductivity.

We have used electrocrystallization as one route to prepare $[Ru(bpy)_3](C_{60})_2$. . In dichloromethane, the half-wave potential for the one-electron reduction of $Ru(bpy)_3^{2+}$ is ca. 300 mV negative of the $C_{60}^{1-/2-}$ wave and 700 mV negative of the $C_{60}^{0/1-}$ wave. Therefore, it is possible to produce either C_{60}^{1-} or C_{60}^{2-} at the electrode surface without reducing the ruthenium complex. Since the dielectric constant of dichloromethane is small (ε_S = 8.93 [10]), we find that $Ru(bpy)_3^{2+}$ ion pairs with electrogenerated C_{60}^{1-} and $[Ru(bpy)_3](C_{60})_2$ crystallizes on the electrode surface.

This process is evident in the cyclic voltammograms (11) shown in Figures 1 and 2. In both cases the solution was saturated with $[Ru(bpy)_3](PF_6)_2$ and was 0.45 mM in C_{60}. Figure 1 shows the first cyclic voltammetric scan where the potential was swept past the first C_{60} reduction wave (A) and into the second reduction wave (B). On the anodic sweep there is cross-over consistent with an increase in active electrode surface area, and the waves corresponding to C_{60}^{2-} (C) and C_{60}^{1-} (D) oxidation are sharp and characteristic of stripping processes (12). The origin of the small shoulder at -1.05 V (E) is currently unknown.

Figure 2 shows the first four voltammetric scans in a more restricted potential range. The scan was started at the foot of the first reduction wave of C_{60} and continued into the second reduction wave. The anodic sweep does not reach potentials sufficiently positive to re-oxidize C_{60}^{1-}. After such continual voltage scans a black crystalline deposit is visible on the electrode surface.

To obtain larger amounts of material required for conductivity and spectroscopic measurements, crystals were grown at a Pt mesh electrode held at -1.1 V for periods between four and six days. In this deposition regime black crystalline needles could be observed growing out from the surface after ca. 12 hours (13). Figure 3 shows a scanning electron micrograph of the $[Ru(bpy)_3](C_{60})_2$ crystals obtained on a Pt electrode after only 13 minutes in the potential hold (-1.1 V) regime (14). The absence of sample charging suggests that the crystals are conductive. We are currently optimizing the electrolysis procedure to grow crystals of sufficient quality for X-ray structure determination.

The composition of the deposited material was evaluated by dissolving it in benzonitrile and taking a visible/near-infrared spectrum of the resulting solution. The near-IR spectra show that the only fullerene anion present is C_{60}^{1-} (15). Also, from the known extinction coefficients for C_{60}^{1-} (λ_{max}=1078 nm) (15) and $Ru(bpy)_3^{2+}$ (λ_{max}= 452 nm) (16), we calculate a 1:2.0 (±0.2)

[Ru $(bpy)_3^{2+}$]: [C_{60}^{1-}] stoichiometry. In addition, X-ray fluorescence measurements did not detect the presence of phosphorus or chlorine in the solid material, indicating that the anion PF_6^- and dichloromethane solvent are not incorporated into the material (14).

Conductivity measurements were conducted on compressed powder samples using a two-point probe method and a cell designed in these laboratories (17). At 25 °C the specific conductivity, σ of the $[Ru(bpy)_3](C_{60})_2$ was found to be 0.01 Ω^{-1} cm^{-1}. The temperature dependence of the conductivity is shown as an Arrhenius plot in Figure 4. A linear relationship is observed over the entire temperature range measured. The increase in σ with temperature is typical for semiconductors. The activation energy was found to be 15.1 ± 0.1 kJ mol^{-1} (0.15 eV). This value is similar to those found in single crystal alkali metal - TCNQ systems (18). No photoconductivity was observed when the sample was illuminated with white light.

We speculate that the high conductivity iis related to electronic overlap between the two ions composing the black solid. We postulate that this overlap involves donation of electron density from the C_{60}^{1-} to the ligand orbitals in the $Ru(bpy)_3^{2+}$ ($\Delta E^\circ \approx 0.7$ V). However, further speculation on the nature of the conductivity and the electronic structure of such transition metal chelate - fulleride materials will have to await future measurements of their structure and properties.

Literature Cited

1. Krätschmer, W.; Lamb. L.D.; Fostiropoulos, K.; Huffman, D.R. *Nature* 1990, 347, 354.

2. Haddon, R.C.; Hebard, A.F.; Rossiensky, M.J.; Murphy, D.W.; Duclos, S.J.; Lyons, K.B.; Miller, B.; Rosamilia, J.M.; Fleming, R.M.; Kortan, A.R.; Glarum, S.H.; Makhija, A.V.; Muller, A.J.; Eick, R.H.; Zahurak, S.M.; Tycko, R.; Dabbagh, G.; Thiel, F.A. *Nature*, 1991, 352, 787.

3. Fleming, R.M.; Ramirez, A.P.; Rosseinsky, M.J.; Murphy, D.W.; Haddon, R.C.; Zahurak, S.M.; Makhija, A.V. *Nature* 1991, 352, 787.

4. Juris, A.; Balzani, V. *Coord. Chem. Rev.* 1988, 84, 85.

5. Wragg, J.L.; Chamberlain, J.E.; White, H.W.; Krätschmer, W.;Huffman, D.R. *Nature* 1990, 348, 623.

6. Electrodeposition has been used to prepare thin films of the tetraalkylammonium salts of the mono- and dianions of C_{60} (7) and the electrochemistry of C_{60} films has been reported (7-9). However, in these studies, the film materials were not isolated in sufficient quantities for further physical characterization. Hence it is not clear that these films are electronically conductive.

7. Koh, W.; Dubois, D.; Kutner, W.; Jones, M.T.; Kadish, K.M. *J. Phys. Chem.* 1992, 96, 4163.

8. a) Jehoulet, C.; Bard, A.J.; Wudl, F. J. Am. Chem. Soc. 1991, 113, 5456.

   b) Compton, R.G.; Spackman, R.A.; Wellington, R.G.; Green, M.L.H.; Turner, J. J. Electroanal. Chem. 1992, 327, 337.

9. Zhou, F.; Yau, S.; Jehoulet, C.; Laude, D.A.; Guan, Z.; Bard, A.J. *J.Phys. Chem.* 1992, 96, 4160.

10. Marcus, Y. *Ion Solvation;* Wiley-Interscience: New York, 1985.

11. Electrochemical measurements were conducted using a Princeton Applied Research 173 Potentiostat and a 175 Universal Programmer. Potentials were measured against an $Ag/AgNO_3$ (0.10 M in dimethylsulfoxide) reference electrode separated from the working compartment by a Vycor® junction.

12. Bard, A.J.; Faulkner, L.R. *Electrochemical Methods: Fundamentals and Applications;* Wiley: New York, 1980.

13. The $[Ru(bpy)_3](C_{60})_2$ compound is moderately air sensitive. Hence the electrocrystallization was carried out in a nitrogen atmosphere glove box (Vacuum Atmospheres, Inc.)

14. Electron microscope images and X-ray fluorescence measurements were obtained using a Philips 505 SEM with a Kevex XRF attachment.

15. Lawson, D.R.; Feldheim, D.L.; Foss, C.A.; Dorhout, P.K.; Elliott, C.M.; Martin, C.R.; Parkinson, B.A. *J. Electrochem. Soc.* 1992, 139, L68.

16. Elliott, C.M.; Hersenhart, E.J. *J. Am. Chem. Soc.* 1982, 104, 7519.

17. The conductivity cell consisted of 0.64 mm diameter Pt electrodes that contacted the powder sample inside a glass capillary tube. The assembly was prepared inside the glove box and sealed with epoxy prior to removal and conductivity measurements.

18. Torrance, J.B. *Acc. Chem. Res.* 1979, 12, 79.

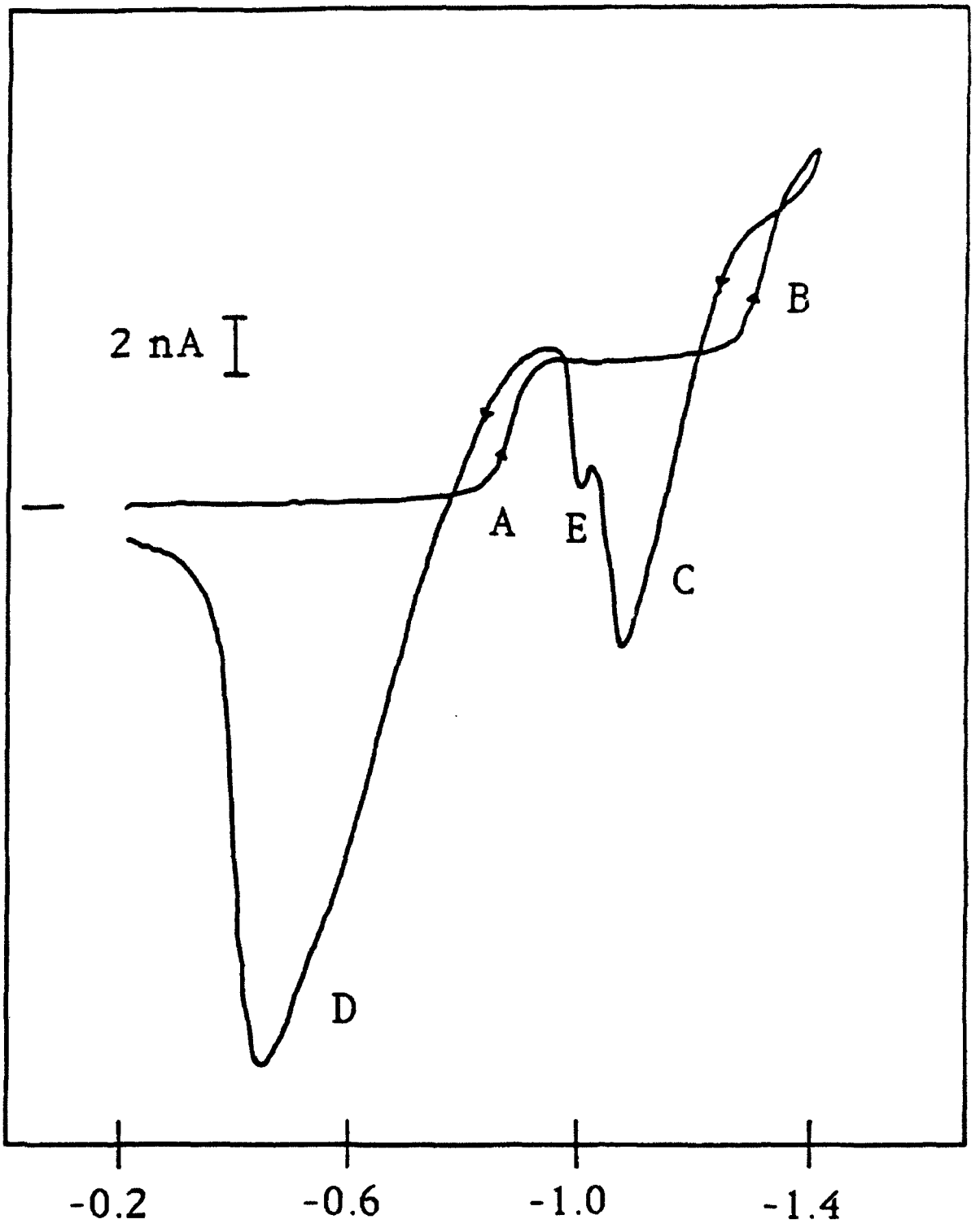
Figure Captions

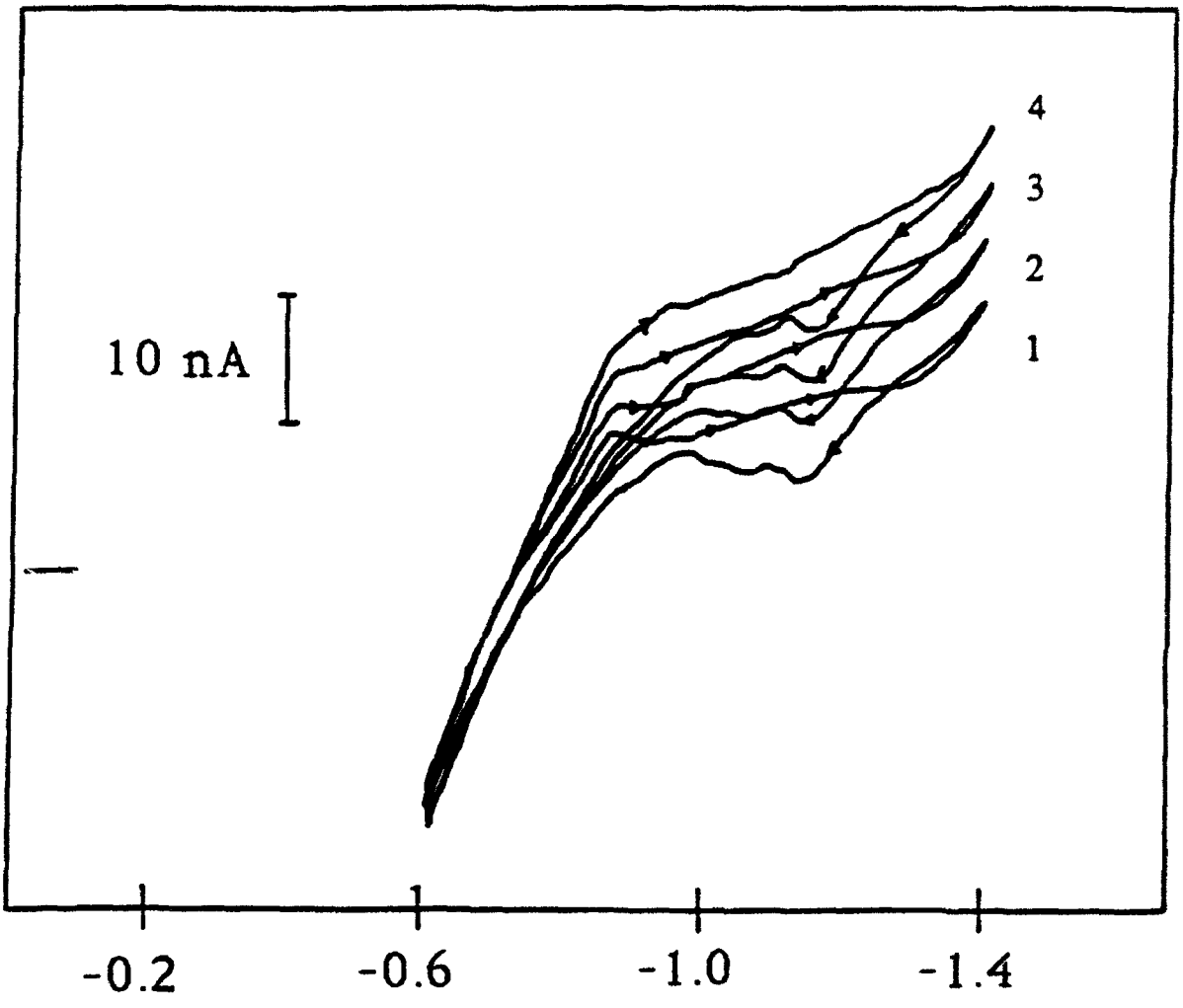
Figure 1. Cyclic voltammogram of 0.45 mM C_{60} in dichloromethane saturated with $[Ru(bpy)_3](PF_6)_2$ (first scan). Scan rate 20 mV sec^{-1}. Pt electrode diameter 125 μm. Potentials measured against Ag/Ag^+ 0.10 M in DMSO.

Figure 2. Cyclic voltammograms showing successive growth of surface deposit. Conditions as given in Figure 1.

Figure 3. Scanning electron microscope image of $[Ru(bpy)_3](C_{60})_2$ crystals formed on Pt electrode after 13 minutes of electrolysis. Scale bar 10 μm. Magnification 4580X. Accelerating voltage 30 kV. Sample was not metal coated prior to imaging.

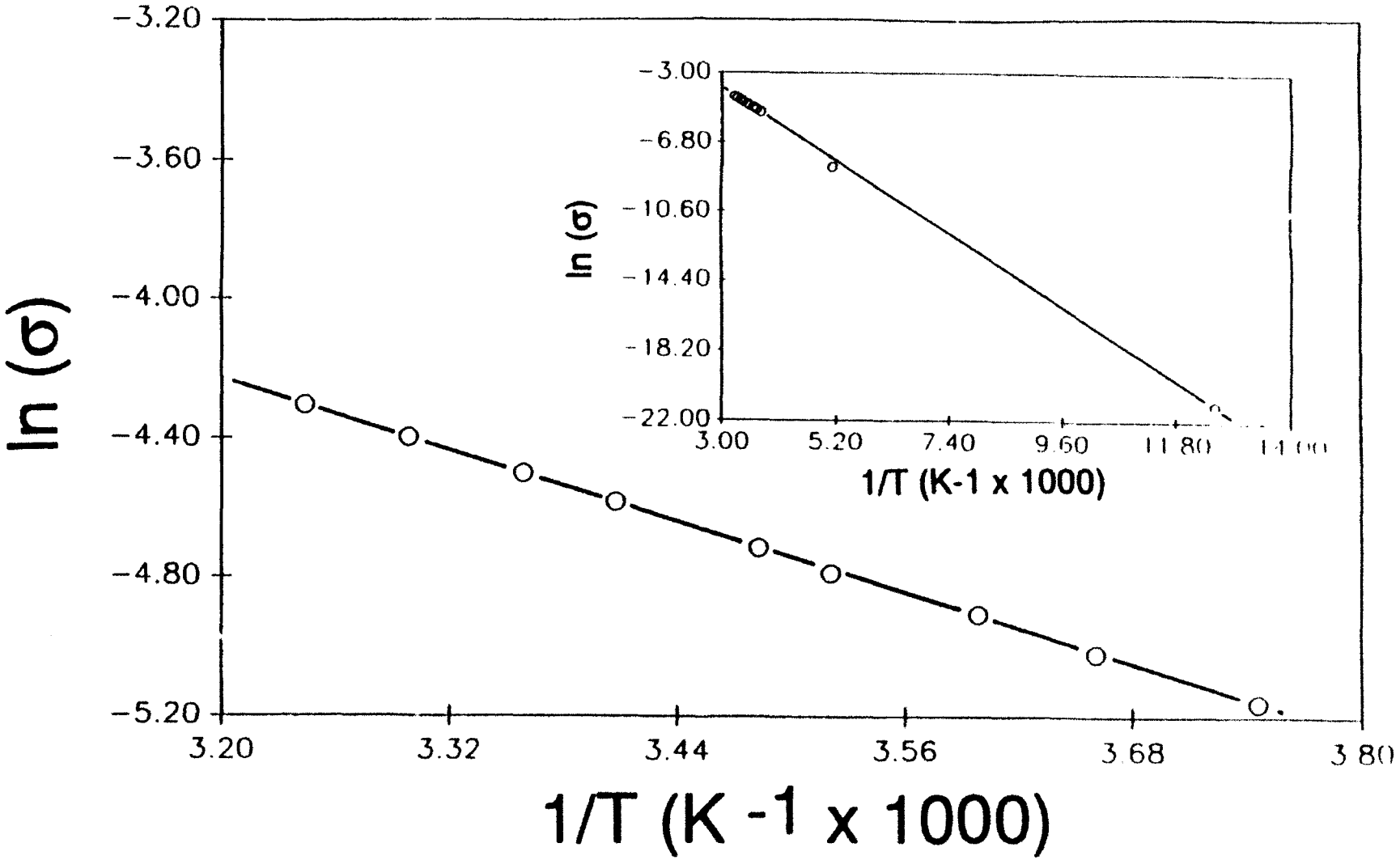
Figure 4. Temperature dependence (1/T) of conductivity (ln σ) of $[Ru(bpy)_3](C_{60})_2$ solid. Temperature range 266.4 K to 308 K. (Inset: inclusion of points at 195 K and 83 K).


2 nA
A
B
C
D
E
-0.2
-0.6
-1.0
-1.4
Volts vs Ag/Ag+ (0.10M in DMSO)



Volts vs Ag/Ag+ (0.10M in DMSO)

10 µm


ln (σ)
-3.20
-3.60
-4.00
-4.40
-4.80
-5.20
3.20
3.32
3.44
3.56
3.68
3.80
1/T (K -1 x 1000)
ln (σ)
-3.00
-6.80
-10.60
-14.40
-18.20
-22.00
3.00
5.20
7.40
9.60
11.80
1/T (K-1 x 1000)